

High Purity NiAl Single Crystals and Composites
by Containerless Automated Processing

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Abstract

Ordered intermetallics such as NiAl are considered candidate materials for high temperature applications provided that the proper combination of room temperature toughness and elevated temperature strength can be developed. To begin to understand the fundamental properties of NiAl, ultra-high purity single crystals of NiAl were produced by directional solidification in the containerless mode for property evaluation. Such material has an extremely low concentration of interstitial elements which results in large improvements in room temperature tensile ductility. In addition, various in-situ reinforcement schemes are evaluated for NiAl-based composites produced by containerless processing. Systems evaluated include the NiAl plus Laves phase and/or refractory metal eutectic systems. Results of initial screening tests which include determination of the room temperature fracture toughness and the 1300 K compressive creep behavior are reported. While these materials are not yet competitive with the superalloys, the recent progress in the performance of NiAl-based in-situ composites is discussed.

Introduction

Containerless processing utilizes induction power to heat, levitate, and constrain a liquid zone to effect directional solidification of the processed material. The levitation zone processing system is operable in oxidizing, reducing, inert, or high vacuum environments permitting the treatment of the liquid zone as an open chemical system. Selected chemical reactions to attain desirable high purity levels can thus be carried out without the thermodynamic limitations involved in using a crucible for liquid containment. Single crystal and directionally solidified composite microstructures are grown from nearly turbulent liquids. The freezing solid-liquid interface is constrained to a position within the levitating electromagnetic field by the control system independent of composition changes and the need for any direct temperature measurement. The dimensions of the zone and location of the freezing interface are determined through image processing software in order to control the propagation of the solid liquid interface and the resulting dimensions of the processed ingot. The temperature and composition of the freezing interface are determined by the phase constitution relationships of the system in question and need not be addressed as control variables (1).

Figure 1 shows a schematic of the current system which has been updated from the previous configuration (2). The updated system provides for parallel processing, allowing the utilization of more extensive and time consuming control software. This arrangement speeds up the frequency of control actions by a factor of six to eight. The system software is also more flexible and comprehensive.

Binary NiAl

Recent effort has involved the growth and examination of high purity single crystals of NiAl. Besides interest in the fundamental properties of the binary material, such information provides a basis for comparison with the properties of current NiAl polyphase "in-situ" composite materials. Typical single crystal specimens are shown in Figure 2.

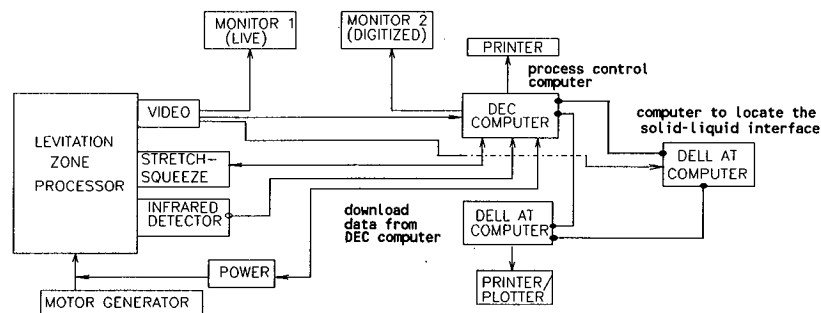


Figure 1: New System Control Layout

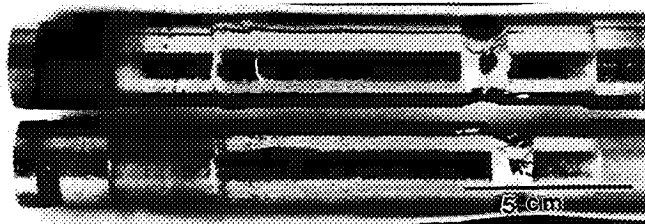


Figure 2: NiAl Single Crystal Specimens.

The effect of interstitial elements on the mechanical behavior of NiAl has become a subject of increasing interest due to some interesting results from recent investigations. These include the attainment of increased ductility in soft orientation single crystals due to minor additions of Fe, Mn, and Ga and the observation of an apparent "strain aging effect" in binary NiAl single crystals (3,4). To begin to understand the possible effects of interstitial elements on the mechanical behavior of NiAl, very low interstitial content NiAl single crystals were produced in the containerless automated system previously described. Interstitial levels were meticulously determined for the directionally zone processed crystals, DS, as well as the starting vacuum induction melted, VIM, precursor ingots used in the containerless DS process. The chemical analyses are summarized in Table 1 along with that of commercially pure material (3,4). The degree of purity is consistent with selected property measurements discussed below.

Table 1: Chemical Analyses of Containerless Zone Processed NiAl Single Crystals and Related Materials, (weight percent).

Material	Carbon	Oxygen	Nitrogen	Sulfur	Comments
VIM Ingot #1	0.0027	0.0037 ^a 0.0040 ^b	0.0004	<0.0010	Typical starting ingot before directional solidification.
VIM Ingot #2	0.0024	0.0042 ^a 0.0046 ^b	0.0003	<0.0010	Typical starting ingot before directional solidification.
HP(b) As-DS	<0.0005	0.0016 ^a 0.0009 ^b	0.0004 ^a 0.0002 ^b	<0.0005	Zone refined ingot (b) from which fracture toughness samples were machined. As-cast.
HP(b) Annealed Crystal	<0.0005	0.0013 ^a 0.0009 ^b	0.0005 ^a 0.0003 ^b	<0.0005	Zone refined ingot (b), annealed 1573 K/3 hrs./air cooled plus 473 K/1.5 hrs./furnace cooled.
HP(b) Annealed Crystal	<0.0005	0.0014 ^a 0.0008 ^b	0.0005 ^a 0.0002 ^b	<0.0005	Zone refined ingot (b), duplicate sample. 1573 K/3 hrs./air cooled plus 473 K/1.5hrs./fc
HP(t) As-DS	<0.0005	0.0011 ^a 0.0006 ^b	0.0002 ^a 0.0001 ^b	<0.0005	Zone refined ingot from which tensile samples were machined. As-cast.
Commercial Purity NiAl Crystals	0.0086 ± 0.0036	0.0058 ± 0.0012	0.0012 ± 0.0002	Not Available	Average composition for crystals reported in Table 1 of the paper by Hack, Brzeski and Darolia, 1993, Scripta Metall. Mater.

^a Analysis performed on a Simultaneous Nitrogen/Oxygen Determinator, LECO Corp., Model TC-136

^b Analysis performed on a Simultaneous Nitrogen/Oxygen Determinator, LECO Corp., Model TC-436

Mechanical test samples were machined from DS material and preliminary properties were determined. The average room temperature fracture toughness for [001] oriented samples with a notch cut parallel to the [011] direction was 11.2 MPa√m, see Table 2. Commercially pure material of the same orientation and fracture geometry had a fracture toughness of 8.3 MPa√m (5). This represents a 35% increase in fracture toughness, apparently due to a decrease in the interstitial levels.

The fracture toughness of the high purity NiAl was also independent of the low temperature heat treatment and was not susceptible to the strain aging effects observed by Hack, et al. (4). However, toughness values determined by Hack et al. were performed on [110] oriented double cantilever beam samples with the notch cut parallel to the [110] direction, a sample geometry and orientation significantly different than that used in the present study. Additional tests on high-purity NiAl are required before a conclusive comparison of low temperature heat treatment effects can be made.

Table 2: Four Point Bend Data from NiAl Single Crystals

Heat treatment	Modulus of Rupture (MPa)	K_{Ic} (MPa√m)
Annealed 1573 K, 3 hr then air cooled	126	11.3
Annealed 1573 K, 3 hr, air cooled + 473 K, 1.5 hr and furnace cooled at 35 K/hr.	126 122	11.4 11.0

In addition to increased fracture toughness, the high purity NiAl also displays a higher tensile ductility compared to material produced by other techniques. At room temperature, near-[123] oriented crystals of high purity NiAl have tensile elongations of 3-5% compared to 1% or less for commercially pure binary NiAl of this or any other crystal orientation (6). In fact, the tensile properties for the high purity NiAl (Table 3) are very similar to those for Fe-doped single crystal NiAl of similar orientation. This would imply that the increased tensile ductility observed in single crystal NiAl as a result of microalloying additions is due to the gettering of interstitial elements.

Table 3: Tensile ductility of single crystal NiAl ([123] orientation)

Heat treatment	0.2% Yield Stress (MPa)	Fracture Stress (MPa)	Tensile Ductility
Annealed 1573 K, 3 hr then air cooled	230.4	297.5	2.4%
Annealed 1573 K, 3 hr, air cooled + 473 K, 1.5 hr and furnace cooled at 35 K/hr.	231.6	341.0	4.72%

Additional studies comparing commercially pure NiAl to high purity NiAl grown at the University of Tennessee have also demonstrated prominent effects of purity on mechanical properties (8,9). For example, the critical resolved shear stress for the U. Tennessee grown material is 25% less than that of material with identical orientation after both materials received identical heat treatments (8). Also, the biaxial bend strength and ductility are significantly greater for the high purity NiAl than for commercially pure material (9). Both observations are consistent with the higher purity of the zone processed NiAl. However, the actual interstitial elements responsible for limiting the mechanical properties of NiAl have not been specifically identified though the most likely suspect might be carbon. Additional testing is underway to identify the specific effects of C, O, and N on the mechanical behavior of NiAl.

In-Situ Composites

Most ordered intermetallic alloys presently being investigated as replacement materials for superalloys are insufficient in two areas; low temperature tensile ductility or fracture toughness and high temperature creep strength. All of the NiAl-based eutectic alloys processed at the University of Tennessee undergo basic screening tests. The key tests are determination of the room temperature fracture toughness and the 1300 K compressive creep behavior of the alloys. All creep testing is performed in air as a secondary check for environmental resistance. If a material

exhibits promising strength at 1300 K then additional creep testing is performed in the 1100 to 1400 K range. Data for alloys studied to date are listed in Table 4.

Table 4: Summary of Creep strength and Fracture Toughness of NiAl Eutectic Alloys

Eutectic System (composition at.%)	Phases Present	Representative Creep Behavior	1300 K Creep Strength (at a strain rate of $1 \times 10^{-5} \text{ s}^{-1}$) (MPa)	Room Temperature Fracture Toughness (MPa $\cdot\text{m}^{1/2}$)
NiAl [001] (Ni-50Al)	β	1100-1300 K: $\dot{\epsilon} = (0.16) \sigma^{5.75} \exp(-314.2/RT)$	19.5	10.7 ± 0.8 (hp) 8.3 ± 0.7 (cp) ^a
NiAl-NiAlTa (Ni-42.75Al-14.5Ta)	β + Laves	1200-1400 K: $\dot{\epsilon} = (4.55 \times 10^{-3}) \sigma^{4.91} \exp(-521.6/RT)$	200.2	5.1 ± 0.8
NiAl-NiAlNb (Ni-41.75Al-16.5Nb)	β + Laves	1200-1300 K: $\dot{\epsilon} = (40.0) \sigma^{4.17} \exp(-414.5/RT)$	148.2	4 ^b
NiAl-Cr (Ni-33Al-34Cr)	β + α	1300 K: $\dot{\epsilon} = (3.52 \times 10^{-23}) \sigma^{7.69}$	137.9	19.2
NiAl-Cr,Mo (Ni-33Al-28Cr-6Mo)	β + α	1200-1400 K: $\dot{\epsilon} = (1.99 \times 10^{-2}) \sigma^{6.37} \exp(-456.6/RT)$	160.4	17 ^c
NiAl-Mo (Ni-45.4Al-9Mo)	β + α	1300 K: $\dot{\epsilon} = (8.59 \times 10^{-18}) \sigma^{5.79}$	81.5	15.2 ± 0.7
NiAl-V (Ni-30Al-40V)	β + α	1300 K: $\dot{\epsilon} = (1.56 \times 10^{-14}) \sigma^{4.88}$	39.8	30.7 ± 3.5
NiAl-Cr-(Cr,Al)NbNi (Ni-27.8Al-33.3Cr-11.1Nb)	β + α + Laves	1300 K: $\dot{\epsilon} = (9.63 \times 10^{-16}) \sigma^{4.52}$	98.8	11.6 ± 3.3
NiAl-Ni ₂ AlZr-V ₂ Zr (Ni-35Al-15V-15Zr)	β + Heusler + Hexagonal	1300 K: $\dot{\epsilon} = (8.79 \times 10^{-6}) \sigma^{2.05}$	9.8	? (probably 2-4)

^aCommercial purity (cp) NiAl:(K.-M. Change, R Darolia, and H.A. Lipsitt, *Acta Metall. Mater* 40, 2727 (1992))

^b(S. Reuss and H. Vehoff, *Scripta Metall. Mater* 24, 1021 (1990))

^c(F.E. Heredia et al., *Acta Metall. Mater* 41, 505 (1993))

Initially two phase eutectics were studied from two family groups. These were NiAl plus Laves phases such as NiAl-NiAlNb and NiAl-NiAlTa and NiAl plus alpha refractory metal eutectic systems such as NiAl with Cr, Mo, or V. The relative merits of these systems are demonstrated in Figure 3, which illustrates a measure of 1300 K creep strength versus room temperature fracture toughness.

As is often the case, those systems that have the best creep strength have the worst fracture toughness and vice versa. The NiAl-Laves phase materials have very good creep strength compared to other NiAl alloys but unfortunately have a fracture toughness of the order of 5 MPa $\sqrt{\text{m}}$. However, 5 MPa $\sqrt{\text{m}}$ is about the average fracture toughness for most polycrystalline NiAl alloys and soft orientation single crystals. Therefore, the large increase in creep strength for the NiAl alloys compared to binary NiAl is not gained at the expense of fracture toughness. The NiAl alpha-phase alloys, on the other hand, exhibit a factor of two or three increase in fracture toughness over that of binary NiAl, but possess only moderate creep strengths. A NiAl-(28Cr,6Mo) alloy has the best balance of properties of any of the alpha alloys studied to date.

While the NiAl-(28Cr,6Mo) alloy displays a reasonable combination of properties (Figure 3), three phase eutectic alloys are also being investigated as a mechanism for designing balanced NiAl-based alloys. One of the first attempts at this concept was the identification and growth of a three phase NiAl-Cr-NiAlNb eutectic alloy. The fracture toughness of this new alloy is intermediate to that of the NiAl-Laves and the NiAl-alpha alloys, but the creep strength was less than anticipated, see Figure 3. The poor creep strength in this case is probably due to its lower melting temperature of 1633 K. Another early attempt at identifying a multiphase composite was that of a three phase material based on the Ni-Al-V-Zr system. This NiAl-Ni₂AlZr-V₂Zr alloy has a remarkable looking and well aligned three phase microstructure, Figure 4. However, since it consists of three brittle intermetallic phases, the fracture toughness is expected to be quite low. Also, due to the V content, the alloy exhibits poor elevated temperature strength as a result of catastrophic oxidation during testing.

None of the alloys in Figure 3 match the Ni-base superalloys for a balance of properties. However, numerous other three phase alloys are presently being investigated in an attempt to tailor the microstructure and properties of new high temperature NiAl-based intermetallic alloys for possible use in high temperature structural applications.

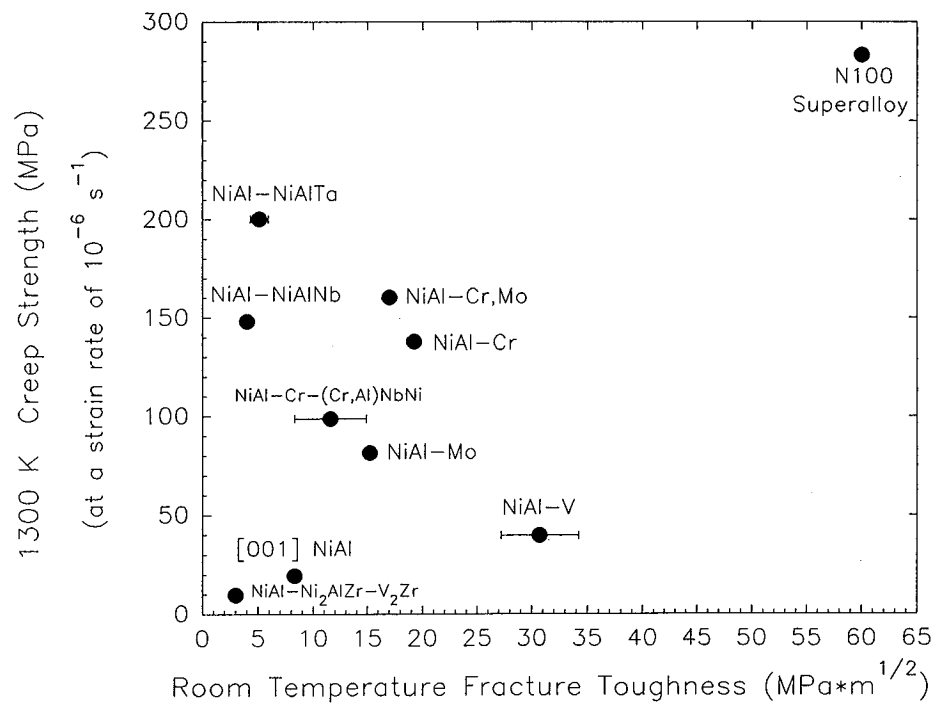


Figure 3: Performance of Various NiAl-Based Eutectic Alloys.

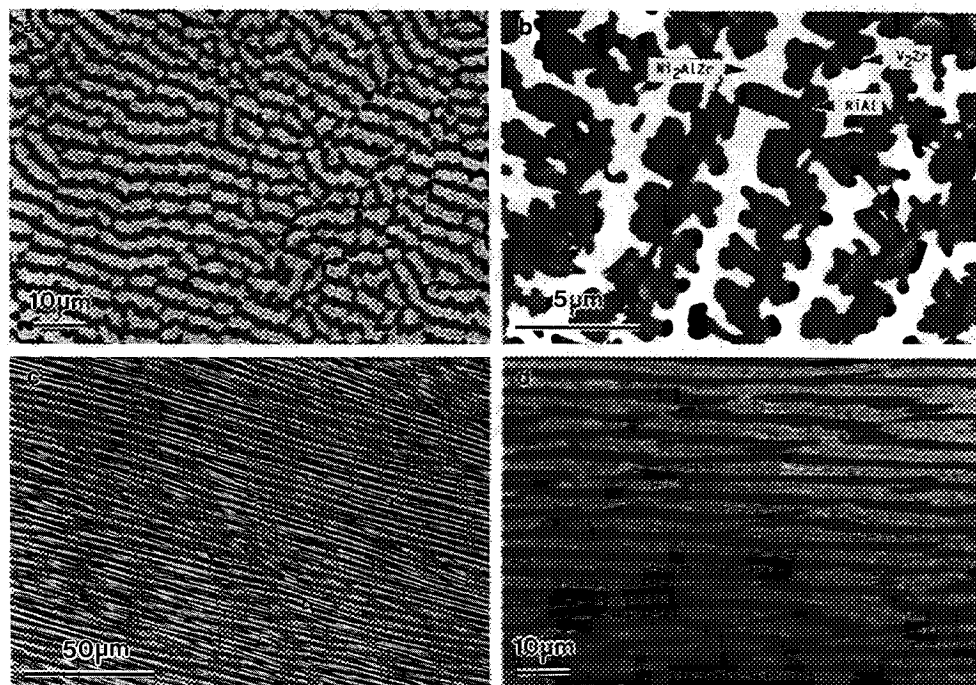


Figure 4: Microstructures of directionally solidified NiAl-Ni₂AlZr-V₂Zr eutectic
 (a) transverse section, optical
 (b) transverse section, SEM backscattered electron image.
 (c) longitudinal section, SEM
 (d) longitudinal section, optical

Summary

1. NiAl of very low interstitial contents can be produced by automated containerless processing.
2. The tensile ductility and fracture toughness of high purity NiAl is greater than that of commercially pure material. Tensile elongations of 5% are possible, similar to that of Fe-doped single crystals.
3. The results suggest that interstitial elements are responsible for limiting the tensile ductility and fracture toughness of binary NiAl.
4. NiAl-based in-situ composites exhibit both increased high temperature creep strength and room temperature fracture toughness over those of binary NiAl.
5. The current level of development of NiAl-based composites are not yet competitive with current superalloys. However, polyphase composites employing Laves, other intermetallic phases, and refractory metals are being examined to enhance the combination of low temperature fracture toughness and high temperature creep strength.

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